Short communication

Recovery and heat treatment of the Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ cathode scrap material for lithium ion battery

Dawei Song [a], Xiaoqing Wang [b], Enlou Zhou [a], Peiyu Hou [a], Fenxia Guo [a], Lianqi Zhang [a,*]

[a] School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300384, PR China
[b] School of Environment and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300387, PR China

HIGHLIGHTS

► Solvent method with inexpensive DMF is used to recover Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ scrap materials.
► The discharge capacity and the cycle life are close to the unused Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$.
► This recovery method is low cost, high purity, high recovery rate and environmental friendly.
► Acetylene black and Al foil can be recovered at the same time with this method.

ARTICLE INFO

ABSTRACT

Sintering method and solvent method are used to recover Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ scrap materials, and the effects of recovery methods and heat treatment on the electrochemical performances for Li-ion battery are investigated in detail. Among these recovered scrap materials, the unheat-treated ones with solvent method display the best electrochemical performances, the discharge capacity and the cycle life are close to that of the unused Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ raw material. Particle size distribution, tap density and recovery rate of scrap materials are also investigated. In addition, acetylene black and Al foil can be recovered at the same time with solvent method.

© 2012 Published by Elsevier B.V.

1. Introduction

The increased demand for Li-ion batteries (LIBs) in recent years has greatly stimulated their production. Except for a large amount of spent LIBs after use, the electrode scraps generated in the production process of LIBs are also increasing dramatically. Therefore, the recovery and recycle of spent LIBs and electrode scraps attract more and more attention. At present, the conventional recovery process of spent LIBs aims at abstracting noble metals (such as Co, Ni and Li) by extraction method, chemical precipitation method and electrolytic method [1–8]. In addition, the electrode scraps (mainly cathode scraps) are recovered and recycled with the similar process and there is not a special recovery and recycle method for the cathode scraps. These conventional methods are widely used, but they may lead to serious resource waste and environmental pollution, these conventional methods are only suitable for the recovery of scraps contained noble metals (such as LiCoO$_2$, Li(NiCoMn)O$_2$), but not suitable for the recovery of LiFePO$_4$ or LiMn$_2$O$_4$ scraps. Considering that the scrap materials of electrodes have not been undergone the charge-discharge process, so they are different from those of spent LIBs, the scrap materials of electrodes can be directly reused only if removing Polyvinylidene Fluoride (PVDF) in scraps with a suitable method. Therefore, developing a new, simply operated, low cost, high purity, high recovery rate and green recovery method of cathode scraps has an important economic and social significance. At present, Li(NiCoMn)O$_2$ materials are one of the cathode materials, and Li[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]O$_2$ material occupies a large proportion of Li(NiCoMn)O$_2$ materials, so the research on recovery method of Li[Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$]O$_2$ scraps is representative for other cathode scraps.

Herein, in order to study the recovery and heat treatment on the Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ cathode scrap material for lithium ion

---

* Corresponding author. Tel./fax: +86 22 60214028.
E-mail address: lianqizhang@126.com (L. Zhang).

battery, sintering method and solvent method with inexpensive *N,N*-Dimethylformamide (DMF) are used to remove PVDF and recover scrap materials from $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ scraps. Structure, morphology, electrochemical performances, particle size distribution, tap density and recovery rate of recovered scrap materials are investigated in detail.

2. Experimental

2.1. Preparation

2.1.1. Sintering method

100 g $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ scraps (from Tianjin EV Energies Co., Ltd.) were sheared into 4 cm^2 size pieces and sintered at 350 °C, 400 °C and 450 °C for 2 h in muffle furnace, respectively. Then, the scrap materials fell off from Al foil by fast stirring mixer. Finally, the recovered scrap materials were sifted out by a 400 mesh screen.

2.1.2. Solvent method

100 g sheared scrap was added into a beaker with 150 mL DMF in batches, and the temperature of DMF was maintained at 70 °C. After stirring for 2 h, a part of sediment was obtained and washed with ethanol after removing Al foil mixtures from solution. Then, the other part of the sediment was collected after washing the obtained Al foil mixtures with ethanol. The two parts of the sediment were dried in air at 100 °C. At last, all the dried sediment was heat treated at 300 °C and 350 °C for 1 h, smashed and sifted out by a 400 mesh screen.

2.1.3. Recovery rate of scrap materials

Part of scrap materials (m_1) can be directly recovered after solvent method. However, part of scrap materials are also lost, that is the scrap materials (m_2) contained in impure Al foil mixtures (m_3). The lost scrap materials (m_2) can be also recovered after dissolving Al foil with excessive NaOH solution. So the recovery rate of scrap materials with solvent method is $m_1/(m_1 + m_2)$, and the purity of obtained Al foil is $(m_3 - m_2)/m_3$.

2.2. Compositional and structural characterization

The crystal structure and surface configuration of the materials were characterized by X-ray diffraction (XRD, Rigaku D/MAX-2500), scanning electron microscope (SEM, JMS-6700F, JEOL) and infrared spectrometer (FTIR-650). Acetylene black content was characterized by element analyzer. The tap density of scrap materials was measured by ZS tap density meter (ZS-201), and the particle size distribution was measured with a particle size analyzer (OMEC, LS-POP (6)).

2.3. Electrochemical measurements

For fabrication of cathode electrodes, the recovered scrap materials (active materials and acetylene black) were mixed with PVDF and complementary acetylene black in *N*-methyl-2-pyrrolidone (NMP), according to the acetylene black content in the recovered scrap materials measured by element analyzer. The slurry for cathodes consisted of 83 wt.% active materials, 10 wt.% acetylene black, and 7 wt.% PVDF. The electrochemical characterization of electrodes was performed using CR2032 coin-type test cells with lithium foil as the anode and 1 M $LiPF_6$ in ethylene carbonate diethyl carbonate (1:1 in volume) as the electrolyte. The cells were charged and discharged between 3.0 V and 4.3 V versus Li by applying a current density of 30 mA g^{-1} at 25 °C.
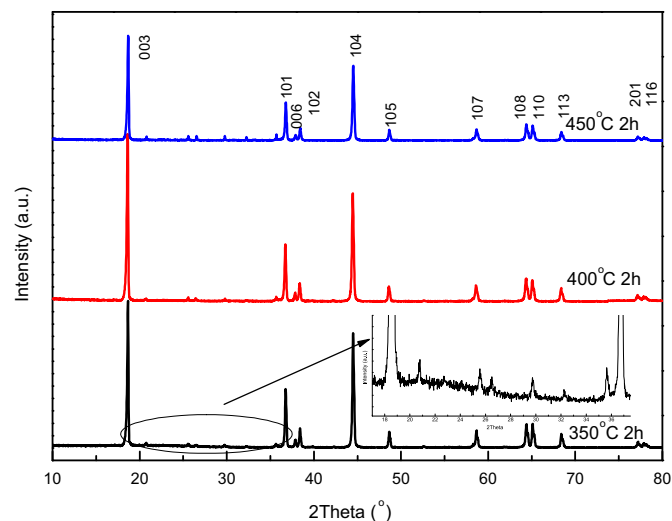

Fig. 1. XRD patterns of the scrap materials sintered at different temperatures.

3. Results and discussion

3.1. Sintering method

Fig. 1 shows XRD patterns of the scrap materials sintered at different temperatures. The appearance of some weak impurity peaks between (003) and (101) at all sintered temperatures demonstrates $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ scrap materials have decomposed during sintering process. In order to find the reason for the decomposition of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$, two contrast experiments are carried out. The mixtures of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ raw material and acetylene black are sintered at 450 °C, but the same impurity peaks do not appear in XRD, indicating that self-decomposition or carbothermal reduction reaction between acetylene black and $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ can not occur at this temperature. The mixtures of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ raw material and PVDF are sintered at 450 °C, and the same impurity peaks appear in XRD, indicating that the impurity peaks are only due to PVDF. An assumption is proposed to explain how the PVDF leads to the decomposition of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ and the appearance of impurity peaks, during the sintering process, PVDF decomposes
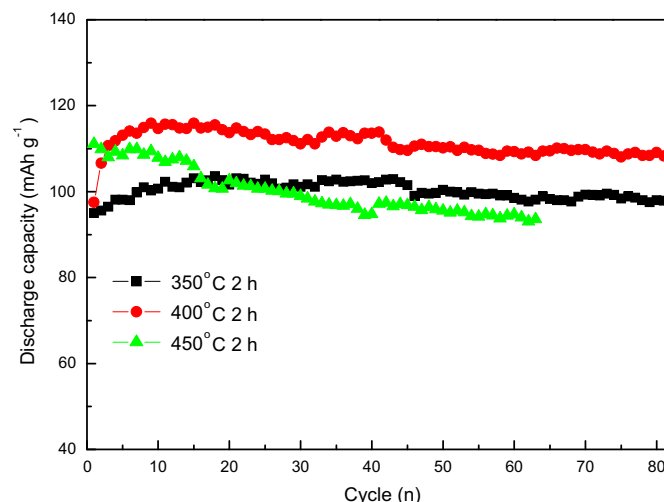

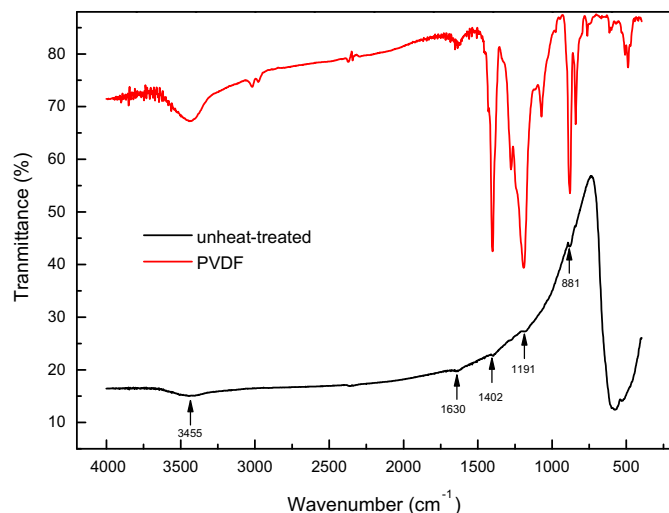**Fig. 2.** Cycle life of the scrap materials sintered at different temperatures.

Fig. 3. IR spectrums of the unheat-treated scrap materials.

into HF, then $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ reacts HF with and generates LiF and impurities (may be nickel cobalt manganese oxide). In order to verify this assumption, scrap materials after sintering are washed with hot water, and saturated $CaCl_2$ solution is used to test F^-. The appearance of white precipitate (CaF_2) verifies that the LiF exits in the scrap materials after sintering, which proves the rationality of the above assumption. But from Fig. 1, only a little $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ decomposes because of HF, the layer structure of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ is not destroyed completely, and there are still some characteristic peaks of layer structure.

The cycle life of the scrap materials electrodes sintered at different temperatures is shown in Fig. 2. The maximum discharge capacity of the scrap materials electrodes sintered at 350 °C is about 103 mAh g^{-1}, but little scrap materials fall off from Al foil, indicating that PVDF has not been removed completely in this condition. The maximum discharge capacity of the scrap materials sintered at 400 °C is about 116 mAh g^{-1}, and most scrap materials fall off from Al foil, indicating that PVDF can be removed in this condition. The maximum discharge capacity of the scrap materials sintered at 450 °C is about 109 mAh g^{-1}, and all scrap materials can fall off from

Al foil. The above results indicate that scrap materials can fall off from Al foil when sintered temperature is above 400 °C, but the discharge capacity is far from the unused $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ materials contained in these scraps (At the same test condition, the discharge capacity of the same batch $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ raw material as the $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ contained in these scraps is about 150 mAh g^{-1}.) and decreases with the increasing of sintered temperature, which is related to the decomposition of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$. Therefore, sintering method is not suitable for the recovery of $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ scrap materials.

3.2. Solvent method

Except for sintering method, solvent method is also an alternative method to remove PVDF in scraps. Common solvents include N-methyl-2-pyrrolidone (NMP), Dimethylacetamide (DMAC) and
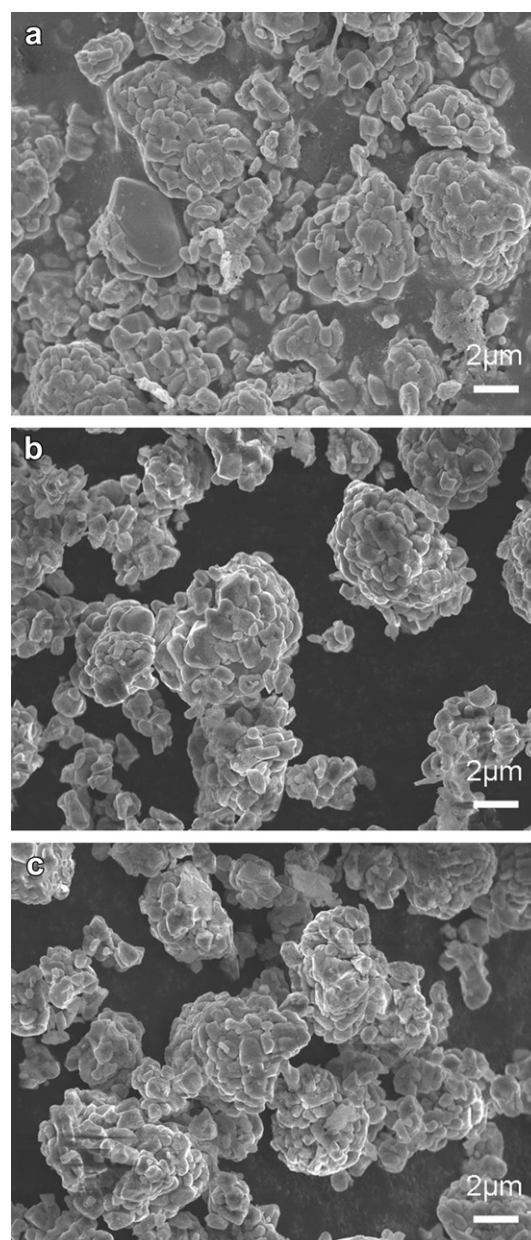

Fig. 5. SEM of the scrap materials heat treated at different temperatures (a) unheat-treated, (b) 300 °C 1 h and (c) 350 °C 1 h.
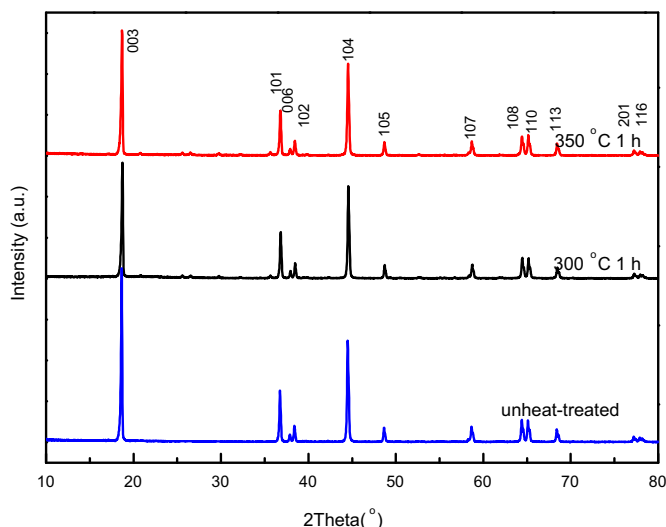

Fig. 4. XRD patterns of the scrap materials heat treated at different temperatures.
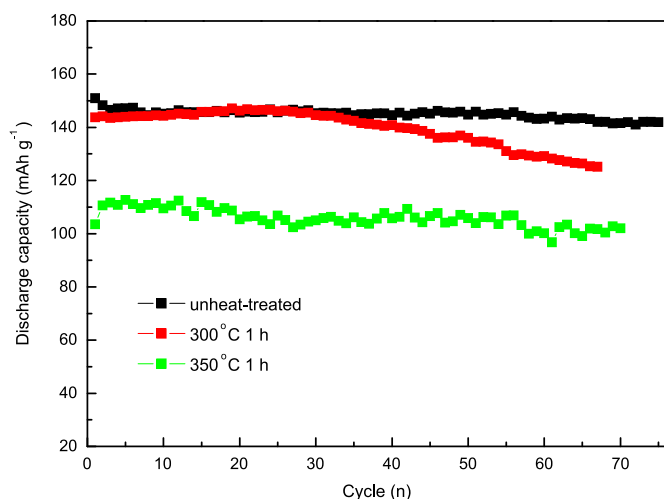
Fig. 6. Cycle life of the scrap materials heat treated at different temperatures.
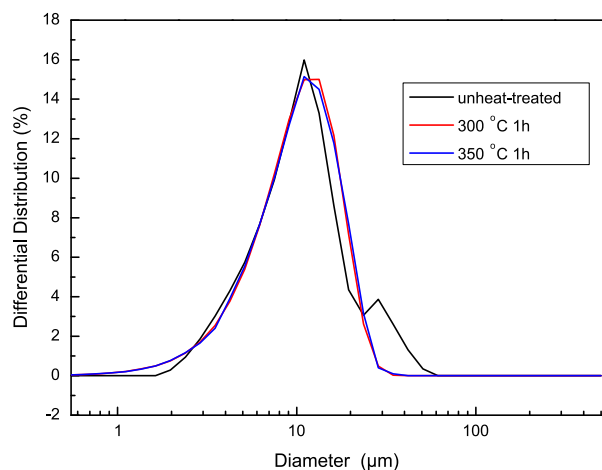
N,N-Dimethylformamide (DMF), but DMF is chosen as solvent to remove PVDF in this experiment for its low cost, high solubility and reusability. Fig. 3 is IR spectrums of the unheat-treated scrap materials recovered with solvent method. It is observed that there are still some small characteristic absorption peaks of PVDF (such as 1630 cm^{-1}, 1402 cm^{-1}, 1191 cm^{-1} and 881 cm^{-1}) in unheat-treated scrap materials, indicating that PVDF is not removed completely with solvent method. In addition, the absorption peaks at 3455 cm^{-1} is due to the remaining structural water. The residual PVDF may lead to agglomeration and average particle diameter increasing of recovered scrap materials, the agglomeration and average particle diameter increasing influence the products quality of recovered scrap materials for sale. In consideration of this, heat treatment at 300 °C and 350 °C is selected to further remove PVDF in the text. The low heat treatment temperature aims to avoid or reduce the reaction between Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ and HF from PVDF.

Fig. 4 shows XRD patterns of the scrap materials heat treated at different temperatures. I_{003}/I_{104} of the unheat-treated scrap materials is 1.713, demonstrating that the unheat-treated scrap materials have typical layer structure. I_{003}/I_{104} of the scrap materials decreases obviously after heat treatment, demonstrating that the layer structure is also destroyed partly. Considering that self-decomposition or carbothermal reduction reaction can not occur at this temperature and PVDF is not removed completely with solvent method, so the main reason for the decrease of I_{003}/I_{104} should be still attributed to the decomposition of Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ which is caused by HF from PVDF.

From SEM of the scrap materials heat treated at different temperatures in Fig. 5, it is obvious that there is a certain degree agglomeration of spherical-like Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ and acety-lene black in the unheat-treated scrap materials, and the agglomeration phenomenon demonstrates PVDF is not removed completely before heat treatment, which is consistent with the IR result in Fig. 3. After heat treated at 300 °C and 350 °C, the agglomeration degree is reduced obviously, which may be related to the removal of PVDF. In addition, the decomposition of some Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ because of HF from PVDF can also lead to the reduction of the agglomeration degree.

Fig. 6 displays the cycle life of the scrap materials heat treated at different temperatures. The discharge capacity of the unheat-treated scrap materials is about 147 mAh g^{-1}, which is close to that of the unused Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ raw material contained in these scraps (about 150 mAh g^{-1}), and the cycle life is also excellent. The discharge capacity of scrap materials heat-treated at 300 °C is about 146 mAh g^{-1}, but the cycle life is poor. The discharge capacity of scrap materials heat treated at 350 °C is only about 110 mAh g^{-1}, which is far from the unused Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ materials. It can be seen that the unheat-treated scrap materials display the best electrochemical performances which are not influenced by residual PVDF, and the heat treatment does not contribute to improve the discharge capacity and cycle life of scrap materials. The results are consistent with the XRD results in Fig. 4.

Except structure, morphology and electrochemical performance, particle size distribution and tap density are also important

μm	D50	D10	D25	D75	D90
unheat-treated	9.48	4.17	6.37	13.14	21.03
300 °C 1 h	9.42	3.99	6.30	12.98	16.56
350 °C 1 h	9.39	3.97	6.27	12.87	16.20

Fig. 7. Size distribution curve of the scrap materials heat treated at different temperatures.
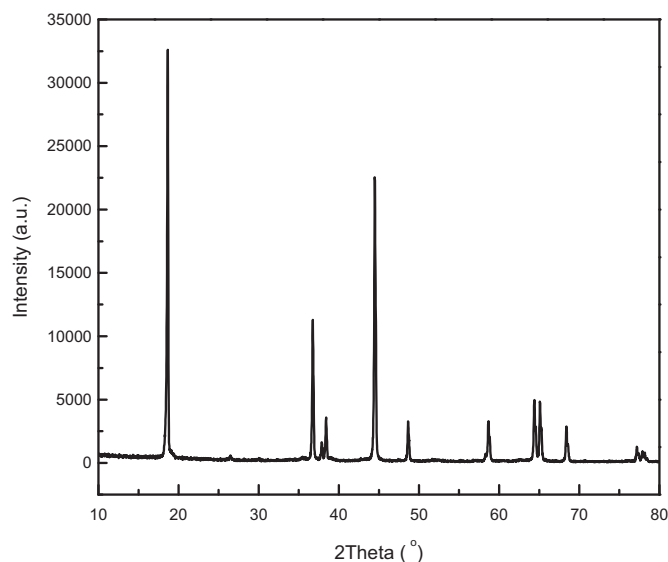
Fig. 8. XRD pattern of the scrap materials obtained from impure Al foil mixtures.

parameters for Li-ion battery cathode materials. Fig. 7 shows the particle size distribution curve of the scrap materials heat treated at different temperatures. In addition to the single distribution peak at about 10 μm, there is a small distribution peak at about 20 μm in the particle size distribution curve of the unheat-treated scrap materials. After heat treated at 300 °C and 350 °C, the small distribution peak disappears and the average particle diameter (D_{50}) decreases slightly. The explanation is the same as SEM in Fig. 5, the small distribution peak may be related to the agglomeration, after heat treated, the agglomeration degree is reduced, so D_{50} decreases slightly.

The tap density of the unheat-treated scrap materials recovered with solvent method is 1.8 g cm^{-3}, which is close to that of the unused Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ raw material with the same amount of acetylene black. This result indicates that the scrap materials recovered with solvent method have the same tap density as commercial products, and meet the demand for the commercial use.

3.3. Recovery rate of scrap materials

In order to investigate the recovery rate of scrap materials, 100 g Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ scraps are recovered with the above solvent method. After the recovery, 55 g scrap materials (active material, acetylene black) and 43 g impure Al foil mixtures (Al foil, active material, acetylene black) are obtained directly. Then 18.33 g scrap materials (active material, acetylene black) are collected from 43 g impure Al foil mixtures after dissolving Al foil with excessive NaOH

solution. From Fig. 8, there is no Al(OH)$_3$ impurity in 18.33 g scrap materials. So the recovery rate of scrap materials = 55/(55 + 18.33) = 75%, and the purity of Al foil = (43 − 18.33)/43 = 57%.

In order to improve the recovery rate of scrap materials, the obtained impure Al foil mixtures are recovered with the solvent method again. After calculation, the recovery rate of scrap materials increases to 88.6% and the purity of Al foil increases to 74.8% after two step recovery processes. It is believed that the recovery rate of scrap materials and the purity of Al foil can be further improved if more step recovery processes are took.

4. Conclusion

Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ scrap materials are recovered with sintering method, but high temperature sintering method leads to low discharge capacity because of the decomposition of some Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$. Therefore, sintering method is not suitable for the recovery of Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ scraps. Except for sintering method, solvent method with inexpensive DMF is also used to recover Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ scrap materials. The discharge capacity of the unheat-treated scrap materials is about 147 mAh g^{-1} and the cycle life is also excellent, which are all close to the unused Li(Ni$_{1/3}$Co$_{1/3}$Mn$_{1/3}$)O$_2$ raw material. The heat treatment can further remove residual PVDF but does not contribute to improve the discharge capacity and cycle life of scrap materials. The recovery rate of scrap materials and the purity of Al foil can reach 88.6% and 74.8% after two step recovery processes. This recovery method with DMF is simply operated, low cost, high purity, high recovery rate and environmental friendly. In addition, acetylene black and Al foil can be also recovered at the same time with this method.

References

[1] L. Li, J. Lu, Y. Ren, X.X. Zhang, R.J. Chen, F. Wu, K. Amine, J. Power Sources 218 (2012) 21–27.
[2] T. Georgi-Maschler, B. Friedrich, R. Weyhe, H. Heegn, M. Rutz, J. Power Sources 207 (2012) 173–182.
[3] L. Sun, K.Q. Qiu, Waste Manag. 32 (2012) 1575–1582.
[4] Y. Pranolo, W. Zhang, C.Y. Cheng, Hydrometallurgy 102 (2010) 37–42.
[5] L. Chen, X.C. Tang, Y. Zhang, L.X. Li, Z.W. Zeng, Y. Zhang, Hydrometallurgy 108 (2011) 80–86.
[6] J. Kang, J. Sohn, H. Chang, G. Senanayake, S.M. Shin, Adv. Powder Technol. 21 (2010) 175–179.
[7] L. Li, J. Ge, R.J. Chen, F. Wu, S. Chen, X.X. Zhang, Waste Manag. 30 (2010) 2615–2621.
[8] J.M. Nan, D.M. Han, X.X. Zuo, J. Power Sources 152 (2005) 278–284.